



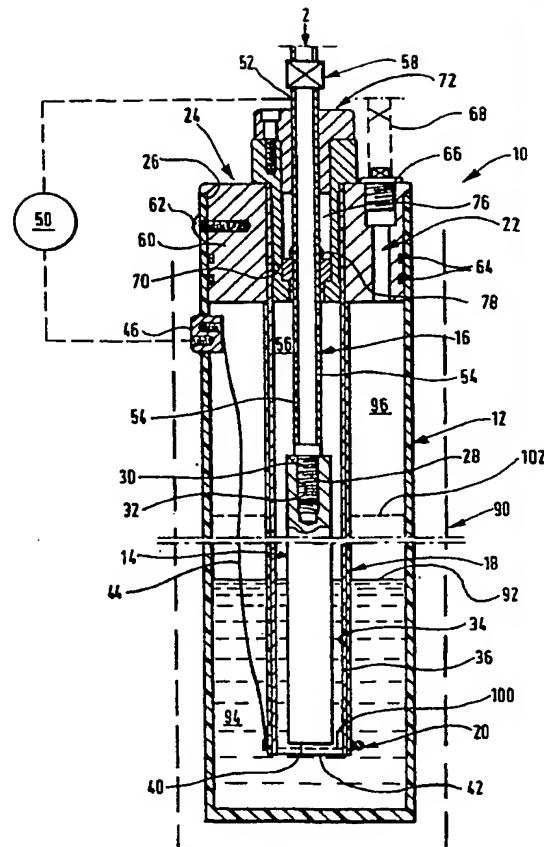
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(54) Title: ELECTROLYTIC CELL FOR THE PRODUCTION OF FLUORINE

(57) Abstract

An electrolytic cell for the production of fluorine is described, the cell comprising: a vessel (12) having therein anode means (14) and cathode means (20), the anode and cathode means being separated by gas separation skirt means (18) extending into and below the surface of an electrolyte contained within the vessel; means for removing hydrogen gas and fluorine gas produced during electrolysis of said electrolyte; wherein the anode means are metal sacrificial anode means and the gas separation skirt means extends below the lowest extent of said anode means.



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5 ELECTROLYTIC CELL FOR THE PRODUCTION OF FLUORINE

The present invention relates to an electrolytic cell for the generation of fluorine.

10 Fluorine gas is presently available from three different sources: compressed fluorine supplied in cylinders; secondary electrolytic fluorine producing cells; and, chemical fluorine generators.

15 A significant disadvantage of compressed fluorine supplied in cylinders is that the fluorine is generally only available diluted with nitrogen or some other diluent gas such as, for example, 20% fluorine in nitrogen. This is due to fluorine being considered too

20 hazardous to transport and/or use as a pressurised pure gas. Cylinder fluorine is convenient to use but safety considerations necessitate the use of expensive gas handling cabinets and piping systems to mitigate the risks involved. Therefore, pressurised fluorine gas

25 cylinders are generally disliked in establishments such as research institutions, e.g. universities and the like. However, if fluorine is needed in such establishments, it is necessary to accept the high risks and costs involved. Many potential users do not proceed with pressurised

30 fluorine once they understand the risks and expense which are entailed.

International patent publication No. WO96/08589 describes a secondary electrolytic cell for the production of

fluorine. The cell describes an "on-demand" secondary electrolytic cell. In this context "secondary" means that once discharged the unit can be recharged with additional hydrogen fluoride electrolyte and reused. The 5 principle of operation is based on the electrolysis of a mixture of hydrogen fluoride and potassium bifluoride described as KF.2HF. By virtue of sensor probes within the cell which determine the presence or otherwise of the electrolyte surface, the user is able to start and stop 10 the delivery of fluorine on demand. Thus, the delivered fluorine gas is at substantially atmospheric pressure. However, such cells as those described in WO96/08589 whilst operating entirely satisfactorily are generally 15 too expensive for users who require less than about 1kg of fluorine per year; most laboratory users falling into this category.

US patent number 3,989,808 describes a method for storing and regenerating pure fluorine by producing a potassium 20 hexafluoroniobate salt which generates fluorine gas on heating. Such fluorine sources are useful for storing very small quantities of fluorine such as about 20g and have the advantages of being safe, easy to use and produce high purity fluorine gas. The chief disadvantage 25 is the high cost and small quantities of fluorine available by this route. Furthermore, the synthesis route for the salt requires several stages and fluorine gas per se is initially required as a raw material. This has to be provided by an electrolytic fluorine cell of 30 some form. Hence, chemical fluorine generators are necessarily expensive and commercial applications are limited to those where high gas purity and safe transportation can justify the high cost.

Prior to World War II, fluorine was largely a laboratory curiosity with relatively limited applications. The Manhattan Project for the development of the atomic bomb suddenly created a need for large quantities of fluorine 5 in order to be able to produce uranium hexafluoride from which enriched uranium is generally produced. The initial methods of producing large quantities of fluorine was by the electrolysis of hydrogen fluoride and potassium bifluoride utilising sacrificial metal anodes 10 composed largely of nickel. Due to the enormous quantities of fluorine being produced, the cells produced were essentially secondary cells wherein the electrolyte was continually replaced and sludge formed by the dissolution of the anode was continuously removed and new 15 anode material continuously or intermittently replaced. Thus, such cells were of huge scale and enormously complex and dangerous. During the Manhattan Project the sacrificial metal anodes were phased out and replaced with carbon anodes which were of much longer life and 20 largely solved the problem of having to remove the sludge caused by dissolution of previously used metal anodes. Since that time, over 50 years and more, virtually all electrolytic cells for the production of fluorine have utilised carbon anodes of one form or another.

25

It is an object of the present invention to provide a relatively inexpensive device for the production of pure fluorine gas, the device being safe and particularly suitable for users who require only relatively small 30 quantities of around 1kg or so per year. A further object of the present invention is to produce a fluorine gas source which is safe to transport. Further objects of the present invention will become apparent as set out hereinbelow.

35

According to the present invention, there is provided an electrolytic fluorine producing cell, the cell comprising: a vessel having therein anode means and cathode means, the anode and cathode means being separated by gas separation skirt means extending into and below the surface of an electrolyte contained within the vessel; means for removing hydrogen gas and fluorine gas produced during electrolysis of said electrolyte; wherein the anode means are metal sacrificial anode means and the gas separation skirt means extends below the lowest extent of said anode means.

Preferably, the cell according to the present invention is a "primary" cell, i.e. a so-called "one shot" device which when exhausted is safely disposed of. In a preferred embodiment, the non-consumable parts of the cell may be recycled. Such cells are generally not amenable to being recharged, for example, with fresh electrolyte or a new anode by the purchaser or user. The cell is used until the electrolyte is exhausted and a new cell is purchased. In this regard the preferred cell according to the present invention is a sealed device which has a vent to take hydrogen away to a fume cupboard for example and a valved fluorine outlet to deliver fluorine to the user's process or experimental apparatus at a rate which is directly proportional to the applied DC current. The user has only to heat the cell to melt the electrolyte which is generally solid at ambient temperatures and apply a power supply to the electrode terminals.

The vessel of the cell according to the present invention is effectively divided into two compartments by the gas separation skirt, these are the fluorine compartment in

which the anode means is situated and the hydrogen compartment which has cathode means.

In one embodiment of the present invention, the gas separation skirt may be a generally cylindrical tube which may be sealed into an upper vessel closure member and extends down into and below the surface of the contained electrolyte, surrounding the anode and extending below the lowest extent of the anode. The fluorine outlet means conducts fluorine gas away from this region via valve means. The skirt may be made of metal which is generally resistant to the effects of fluorine such as steel for example or from a suitable plastics material. In one embodiment, the skirt may be formed from metal and have an electrically insulating plastics material layer thereon which will be explained further herein below.

The cell of the present invention provides a simple, inexpensive but highly reliable device for providing pure fluorine gas on demand. If the user wishes to restrict or stop the flow of fluorine, all that is necessary is that the fluorine outlet valve is restricted or closed. The effect of this is that the fluorine gas generated at the anode exerts a slight pressure on the surface of the liquid electrolyte contained within the gas separation skirt and slowly depresses the level of electrolyte in the fluorine generating compartment where the anode is situated. There is a corresponding rise in the electrolyte level in the hydrogen compartment caused by the displacement of the electrolyte from the fluorine compartment. Once the level of electrolyte in the fluorine compartment reaches the bottom of the anode further electrolysis is not possible and so gas production ceases. The pressure at which gas production

ceases within the anode compartment may be controlled to pressures in the range 1-100cm water gauge by virtue of adjusting the length of the anode and the height and diameter of skirt and cell body.

5

In the cell according to the present invention, the anode is a sacrificial metal anode comprising any suitable metal such as nickel for example. Although the precious metals such as platinum or palladium are technically feasible, they are practically too expensive.

In a normal secondary electrolytic fluorine cell, i.e. a cell where the electrolyte may be recharged and embodying a carbon anode, the above method of operation is not practicable due to the high applied voltage that must be employed with a carbon anode. Secondary fluorine cells incorporate a carbon anode to give reliable operation over a long period of time typically 3000-10000 hours. The anode has to survive many hydrogen fluoride recharge cycles and carbon is the only known material which can survive such duty. However, the carbon survives due to the formation of a protective carbon polyfluoride layer on the surface which has the unfortunate side effect of being an electrical resistor. Thus, in a typical secondary fluorine cell operating at an applied voltage of 10 volts, the potential drop across the polyfluoride layer is typically 3 volts at a current density of only 1500 Am^{-2} . Since in all conventional cells the anode of necessity extends considerably below the gas separation skirt, the gap between the anode and cathode is large typically in the region of 30-40mm so as to obviate the possibility of explosive recombination of fluorine and hydrogen generated below the bottom of the gas separating skirt. Hence, for the reasons given above, it is not practicable to operate a conventional secondary fluorine

cell with the carbon anode shorter than the gas separating skirt. When such a geometry has been tried, it has been found that a negligible current is achieved at an applied potential of 10 volts DC. If the potential is increased to, for example, 15 or 20 volts DC, then the current begins to flow at normal levels and fluorine is generated. However, much of the current flow is due to the formation two bipolar cells whereby the outside of the gas separating skirt is at a negative potential and the inside is at a positive potential. Thus, significant quantities of both fluorine and hydrogen are generated in the fluorine compartment and the same occurs in the hydrogen compartment producing explosive recombination of the two gases. Thus, such a system does not work.

15

However, in the present invention, the sacrificial metal anode exhibits a negligible over potential, since no resistive surface layer is formed, and so can allow a useful amount of current to flow without operation at high cell potentials and consequently avoids the bipolar cell formation with the explosive recombination of generated gases. The anode slowly corrodes away but nonetheless lasts until all of the available fluorine in the hydrogen fluoride electrolyte is depleted to a level whereby no further fluorine can be generated, i.e. about 38%W/V.

In one embodiment of the present invention, the cathode may be an annular metal ring attached adjacent the lower end portion of the gas separating skirt and insulated therefrom as mentioned above. Since the anode does not protrude below the lower end of the skirt, all fluorine is produced at a level above the lowest extent of the gas separating skirt and thus cannot physically reach and recombine with the hydrogen generated at the cathode

which is preferably situated slightly above the lowermost end of the gas separation skirt.

In conventional fluorine cells, the cathode has generally 5 been formed by the inner wall of a steel or cast iron containment vessel. The vessel of the cell according to the present invention may also be made of metal and form the cathode. However, where the cathode is formed as described above, the vessel may alternatively be formed 10 of a plastics material such as PVDF for example, thus further reducing weight and possible contamination of the electrolyte due to corrosion products from the metal and consequently of the fluorine produced.

15 Where the vessel is a plastics material, the cathode may be formed of a metal ring fixed in the base of the vessel for example.

In the present invention, where the cathode is mounted 20 directly on the gas separating skirt and insulated therefrom, the shortest possible current path is provided between anode and cathode without the possibility of recombination of hydrogen and fluorine.

25 In a second embodiment of the present invention, the cell vessel may be made of metal such as carbon steel, stainless steel or Monel metal (trade name) for example and the anode may be in the form of a disc having a plane normal to the axis of the cell. In this embodiment, the 30 cell vessel inner wall forms the cathode. Due to the increased area of the anode adjacent the lower end of the gas separation skirt, substantially increased current flow at reduced or low voltages have been found. However, the lowest extremity of the anode in this second

embodiment is still above the lower end of the gas separation skirt.

Another feature of the present invention the possibility 5 of a purge system for the fluorine compartment prior to generation of fluorine. This allows a user to purge out the fluorine compartment before and after use. This is particularly important in some applications where oxygen may be a contaminant. The purge tube preferably passes 10 through the hydrogen compartment and has an outlet which is positioned below and directed towards the fluorine compartment. In this way, it is not possible for any fluorine to inadvertently leak to the outside through the purge tube as there is no direct access to the purge tube 15 from the fluorine compartment. Any suitable gas such as nitrogen, helium or argon for example may be used as the purge gas.

A very important advantage of a primary cell according to 20 the present invention is that being sealed it may be shipped to customers by air. This is banned by International regulations for fluorine contained in pressurised cylinders and secondary devices are too massive for economic transportation by air. Thus, this a 25 further benefit of the cell of the present invention since in a secondary cell, the user has to charge the cell with anhydrous hydrogen fluoride which is itself a very hazardous chemical.

30 A further important advantage of the cell according to the present invention, due to the use of a sacrificial metal anode is related to the purity of the fluorine produced. In conventional cells utilising carbon anodes, the fluorine gas is contaminated with carbon 35 tetrafluoride (CF₄) and other fully or partially

fluorinated carbon-fluorine compounds. Furthermore, the use of a metal anode in the cell of the present invention allows the use of high purity electrolyte which can be used to prepare high purity fluorine directly by 5 electrolysis. This is not a practical proposition in a conventional secondary fluorine cell, partly due to the CF_4 mentioned above, but also because high purity electrolyte is known to cause problems in the operation of secondary fluorine cells. This is due to the fact 10 that the carbon anodes depend on the presence of various metal ions (including but not limited to nickel and lithium) in the molten electrolyte to avoid the problem of the "anode effect". The so-called anode effect is caused by excessive build-up of carbon polyfluoride on 15 the anode surface which in turn causes the operating current to decline significantly even if the applied potential is increased, so-called "polarisation". This is a significant operational problem in conventional secondary cells but from which the sacrificial anode in 20 the present invention is completely free. A further problem with conventional secondary cells is that in order to avoid the above described anode effect and polarisation, it is necessary to ramp-up the cell to its 25 full current capacity very slowly, e.g. between 20 minutes and 1 hour starting at about 10-20% of full current. This is very inconvenient when a cell is being used for intermittent fluorine supply or on an "on-demand" basis. The cell of the present invention may be brought to full current in a period of only 1 to 2 30 seconds and may be switched on and off as frequently as may be desired within the life of the sacrificial anode without any adverse effect on operation or reliability.

As explained above, in conventional secondary fluorine 35 cells the vessel is normally constructed from metal such

as carbon steel or Monel (trade name) metal. This is made cathodic to reduce corrosion and also form the cathode of the cell. However, metal ions which form volatile fluorides, e.g. molybdenum, chromium and tungsten, are 5 slowly leached from the metal by the hydrogen fluoride electrolyte which then react with the fluorine gas in the anode compartment to introduce gaseous metal fluoride contaminants in the resulting fluorine product. The use of the separate metal ring cathode and a plastics 10 material vessel such as PTFE or PVDF obviates the problem of leached metal ions and the production of gaseous metal fluorides contaminating the fluorine product.

A yet further advantage of the cell of the present 15 invention is that the available weight of fluorine from a given weight of electrolyte is significantly increased because the upper hydrogen fluoride concentration may be increased and the lower hydrogen fluoride concentration may be decreased when compared to conventional secondary 20 fluorine cells. Carbon anodes start to disintegrate when the hydrogen fluoride concentration is above approximately 43% W/V. However, the sacrificial metal anode used in the primary fluorine cell of the present invention is able to operate satisfactorily at more than 25 46% W/V. Similarly, at hydrogen fluoride concentrations of below 39% W/V, carbon anodes exhibit a phenomenon known as "polarisation" whereby the current decline sharply and fluorine generation is reduced or ceases completely. The metal anode in the cell of the present 30 invention operates satisfactorily at less than 37% W/V hydrogen fluoride. Thus, the capacity of the cell of the present invention to generate fluorine is at least double that of a conventional secondary fluorine cell of comparable size and electrolyte inventory. This is a 35 significant advantage and makes the fluorine cell of the

present invention lighter and more compact for transportation benefits.

A still further advantage of the present invention is
5 that complex carbon anode constructions are necessary in conventional secondary fluorine cells to connect the carbon anode to the metal cell electrodes. Such constructions are necessary to prevent corrosion at the junction between the carbon anode and metal connection
10 portions. In the present invention the anode hanger and electrical connection is metal to metal welded, providing good electrical contact. The anode is also hollow and simultaneously acts as the fluorine outlet conduit. This feature avoids the need for a separate fluorine outlet
15 pipe which would otherwise increase the diameter and hence the size of the unit.

A still further advantage of the cell of the present invention is that the purity of the fluorine gas is
20 substantially constant for the life the cell. In a conventional secondary fluorine cell there is a regular addition of hydrogen fluoride electrolyte which may introduce water and sulphur compounds which give rise to contaminants in the fluorine such as SF₄, SF₆, SO₂F₂ and
25 OF₂. In the cell of the present invention the electrolyte may be purified before it is put into the cell and the cell is then sealed. Thus, contaminants cannot be introduced during operation or recharging and the fluorine purity is constant and can be guaranteed in
30 the same way as a cylinder of fluorine.

The majority of the components of the cell according to the present invention may be manufactured from suitable plastics materials such as PVDF, for example, which are
35 both economic and easily formed.

The cell according to the present invention may be supplied with a reusable heating jacket such as an electrically heated blanket or water bath for example.

5

In order that the present invention may be more fully understood, an example will now be described by way of illustration only with reference to the accompanying drawings, of which:

10

Figure 1 shows a section in elevation of a cell according to the present invention;

15 Figure 2 is a view in the direction of the arrow 2 shown in Figure 1;

Figure 3 which shows a section similar to Figure 1 of a second embodiment of a fluorine cell according to the present invention; and

20

Figure 4 which shows a plan view of the top of the cell of Figure 3.

25

Referring now to Figures 1 and 2 of the drawings where a fluorine cell according to the present invention is shown generally at 10. The cell comprises a vessel 12 made of a plastics material such as PVDF, a sacrificial metal anode 14 made of nickel, a fluorine outlet conduit 16 to which the anode 14 is connected, a cylindrical gas separation skirt 18, a cathode 20, hydrogen venting conduits 22 and an end closure arrangement 24 to seal the open end 26 of the vessel 12. In order to lend scale to this particular embodiment, the overall height of the cell 10 is about 0.5m. The anode 14 is connected to the fluorine outlet tube 16 by means of co-operating male and

female screw threads 28 on a spigot 30 on the fluorine outlet tube and a recess 32 in the end of the nickel anode 14. The gas separation skirt 18 comprises an inner cylindrical member 34 made of a suitable metal such as 5 carbon steel or copper/nickel alloys, for example, and an outer insulating layer 36 of a suitable plastics material. As may be seen from Figure 1, the end 40 of the anode 14 terminates above the lowest extent 42 of the gas separation skirt 18. The cathode 20 is a steel ring 10 clamped on and adjacent the lower end 42 of the gas separation skirt 18. An electrical conductor 44 extends between the cathode ring 20 and a terminal connector block 46 sealed into the vessel wall for the connection of a 5amp 10 volt DC power supply 50, the anode 15 connection 52 being made to the Monel metal (trade mark) or stainless steel fluorine outlet conduit 16. The outlet conduit 16 is provided with holes 54 to conduct fluorine gas away from the anode compartment 56 via a regulating valve 58 on the end of the fluorine conduit 20 16. The vessel closure assembly 24 comprises a main plug member 60 fixed into the open end of the vessel 12 by means of screws 62 and sealed thereto by 'O' ring seals 64. The hydrogen venting conduits 22 are formed through 25 the plug member 60 and provided with seal plugs 66 for use in transportation of the cell and which may be replaced by a valved conduit indicated by the dashed line 68 when in use. The gas separation skirt 18 is received in a central bore 70 of the plug member 60. A gland sealing arrangement 72 seals the bore of the gas 30 separation skirt metal member 34 from the ambient atmosphere and also seals the fluorine take off conduit 16 from the ambient atmosphere. A space 76 is filled with compressible gland sealing material such as expanded PTFE for example. An olive 78 is fixed to the fluorine 35 outlet conduit 16 so as to locate the lowest extent 40 of

the anode 14 relative to the end 42 of the gas separation skirt 18.

As may be seen from Figure 1, the lowest extent 40 of the 5 anode is above the lowest extent 42 of the gas separation sleeve 18. Similarly, the cathode 20 is fixed so that it is slightly above the lowest extent 42 of the gas separation skirt and is insulated from the metal member 34 by the plastics material layer 36.

10

To operate the cell, it is placed in a heating device indicated generally by the dashed line 90 and which may be a water or oil bath for example. The temperature of the cell is brought to between 75 and 100°C (preferably 15 85°C) and allowed to come to temperature equilibrium with the heating device. Once the electrolyte is molten and has reached a temperature equilibrium with the heating device, the cell is purged with nitrogen gas through the outlet valve 58 and pipe 16. The 5 amp, 10 volt DC power 20 supply 50 provided for the purpose is connected between the terminal block 36 and the connection 52 on the fluorine outlet pipe 16. Upon energising the power supply, fluorine is generated at the anode and rises into the anode compartment 56 above the surface 92 of the 25 electrolyte 94, hydrogen is generated at the cathode 20 and rises into the cathode compartment 96 where it may be vented away via the conduit and valve 68 and safely disposed of. The fluorine is generated at a rate which is directly proportional to the applied DC current. If 30 the user restricts or fully stops the flow of fluorine by closing the valve 58, the fluorine in the fluorine compartment 56 exerts a slight pressure on the liquid electrolyte 94 in the anode/fluorine compartment and thus slowly depresses the level of electrolyte such that it 35 eventually extends below the lowest extent 40 of the

anode 14 to a position indicated by the dashed line 100. The level of the electrolyte in the cathode compartment 96 rises to a level indicated by the dashed line 102. At this point, electrolysis stops and consequently, 5 generation of fluorine also stops. Thus, the generation of fluorine may be started and stopped at will, i.e. "on demand" by the user.

Figures 3 and 4 show a second embodiment 110 of a 10 fluorine cell according to the present invention. In this embodiment, the vessel 112 is made of carbon steel, stainless steel or preferably Monel metal (trade name) and the inner wall 114 thereof forms the cathode of the cell. The centrally disposed anode 116 comprises a nickel alloy 15 tube 118 having fluorine tapping holes 120 into the central bore 122 for taking off fluorine and an active anode portion 126 in the shape of a horizontally disposed disc having holes 130 therethrough to allow fluorine gas to pass up into the fluorine compartment 132. The gas 20 separation skirt 136 comprises an insulated tube portion 138 and a lower bell-mouthed portion 140 surrounding the disc anode 126. A spacer 142 is provided at the lower end of the skirt 136 to ensure that the skirt remains centrally disposed in the vessel 112 and cannot touch the 25 inner wall 114. A pressure release valve 150 is provided in the hydrogen compartment 152 to prevent any unwanted build-up of pressure within the compartment for any unforeseen reason. A purge tube 156 is connected to a union 158 at the top and anchored to a block of plastics 30 material 160 at the lower end thereof to form an upwardly directed gas stream 162 directed towards the fluorine compartment 132 for purging purposes the union 158 may be connected to a suitable gas supply such as nitrogen for example for purging before and after use if desired. The 35 base of the cell is fitted with a plastics material disc

164 to ensure that no hydrogen can be formed below the fluorine compartment. Fluorine is extracted from a valve arrangement 166 at the top of the anode tube 118. Electrical connections are made to the anode tube 118 and 5 to screwed post 168 for the cathode which, with other radially directed dowels 170 secure the top block 172 and gland assembly 174 to the vessel 112.

10 The cell of Figures 3 and 4 operates in substantially the same manner as that of Figures 1 and 2.

15 If for any reason the fluorine outlet becomes blocked in either embodiment, the level of electrolyte is depressed below the anode electrolysis and fluorine production ceases.

20 The various features of each embodiment may be interchanged as desired. For example, the gas purge tube of Figures 3 and 4 may be fitted to the embodiment of Figures 1 and 2. Similarly, the cathode of Figures 1 and 2 may also be employed with the separation skirt and anode arrangement of Figures 3 and 4.

25 Due to the geometry of the anode, cathode and gas separation skirt, it is impossible for the generated fluorine and hydrogen to reach each other and recombine.

30 Since the cell does not contain fluorine and may have an electrolyte inventory of 2kg it can be legally and safely transported by air, which is not possible with compressed fluorine in cylinders.

The fluorine gas produced contains about 5%v/v HF. However, this can be simply and easily removed by means

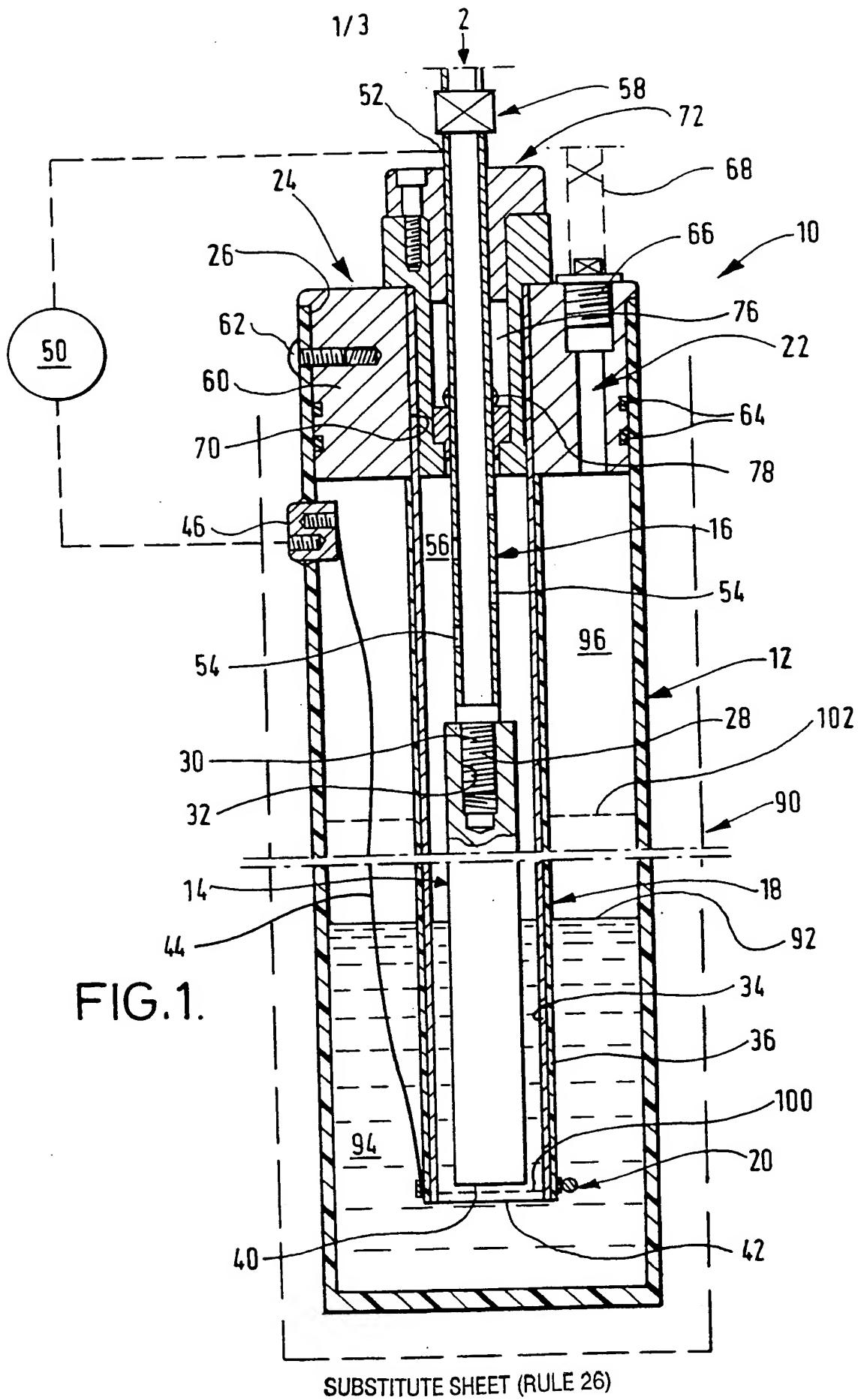
such as absorption onto sodium fluoride. Thereafter, the purity of the fluorine gas produced is high and constant.

5 The quantity of fluorine produced from a given weight of electrolyte may be up to twice that available from conventional secondary cells.

CLAIMS

1. An electrolytic cell for the production of fluorine, the cell comprising: a vessel having therein anode means and cathode means, the anode and cathode means being separated by gas separation skirt means extending into and below the surface of an electrolyte contained within the vessel; means for removing hydrogen gas and fluorine gas produced during electrolysis of said electrolyte characterised in that the anode means are metal sacrificial anode means and the gas separation skirt means extends below the lowest extent of said anode means.
- 15 2. A cell according to claim 1 wherein the cell is a primary cell as hereinbefore defined.
3. A cell according to either claim 1 or claim 2 wherein the cathode is metal and is mounted adjacent a lower end of the gas separation skirt means.
- 20 4. A cell according to any one preceding claim wherein the cathode is mounted on the gas separation skirt means.
5. A cell according to any one preceding claim wherein the cathode is mounted slightly above the lower end 25 of the gas separation skirt means.
6. A cell according to any one preceding claim wherein the cathode is annular in shape and conforms to the cross sectional shape of the gas separation skirt.
7. A cell according to any one preceding claim wherein 30 the gas separation skirt means is generally tubular in form.
8. A cell according to any one preceding claim wherein the gas separation skirt means comprises a metal tube having a layer of plastics insulating material 35 thereon.

9. A cell according to any one preceding claim wherein the vessel is made of a plastics material.
10. A cell according to any one preceding claim wherein the anode is in the form of horizontally disposed disc.
- 5 11. A cell according to any one of preceding claims 1, 2 or 10 wherein the cathode is formed by the inner wall of a metal vessel.
12. A cell according to any one preceding claim wherein 10 the anode material is selected from a metal or alloy of at least one of the group comprising: nickel, iron, copper, platinum and palladium.
13. A cell according to any one preceding claim wherein 15 the fluorine outlet means is a perforated conduit which is substantially coaxial with the anode.
14. A cell according to claim 13 wherein the fluorine outlet conduit also forms the electrical connection to the anode.
15. A cell according to any one preceding claim wherein 20 closure of the fluorine gas outlet conduit means causes the surface level of the electrolyte in an anode compartment to be depressed below the lower end of the anode and so terminate fluorine gas production.
- 25 16. A cell according to any one preceding claim wherein there is conduit provided to enable the fluorine compartment to be purged with a gas.
17. A cell according to claim 16 wherein the conduit is routed through the hydrogen compartment to direct a 30 stream of purge gas upwardly into said fluorine compartment.



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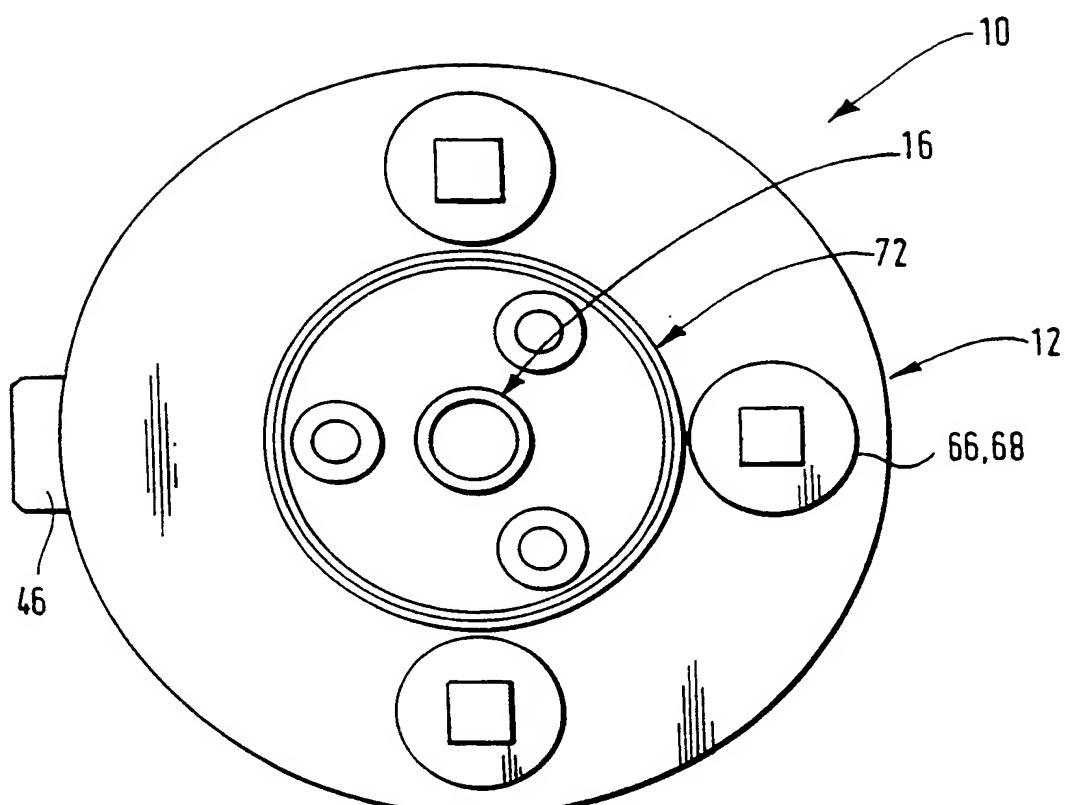


FIG. 2.

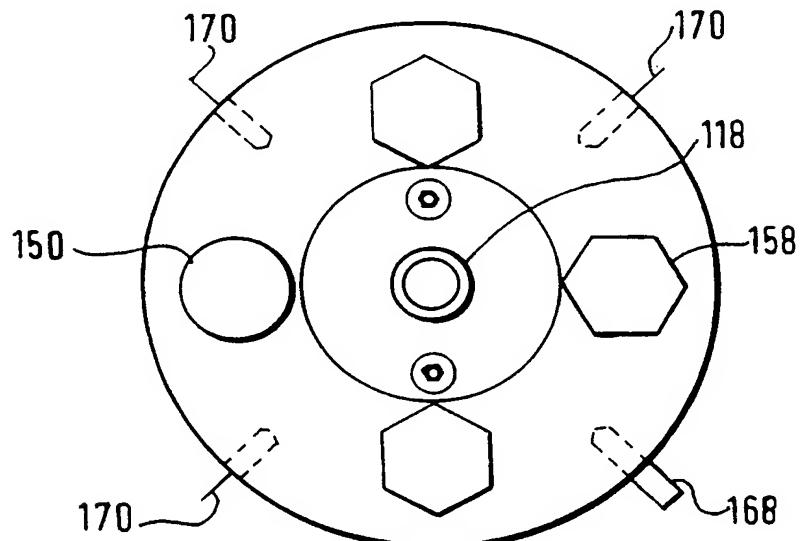
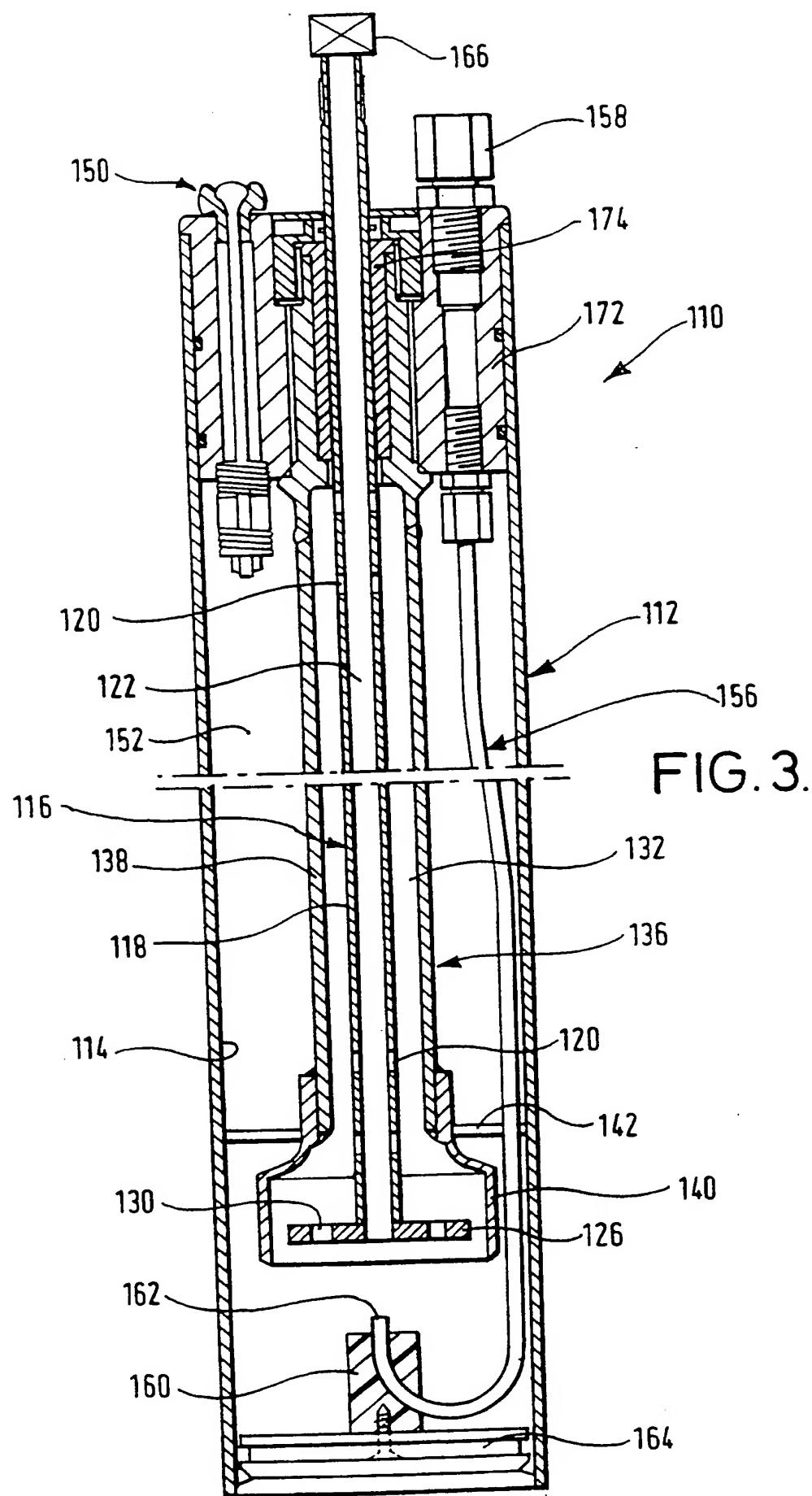


FIG. 4.

SUBSTITUTE SHEET (RULE 26)



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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/03494

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C25B9/00 C25B1/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>GB 425 979 A (E.I. DU PONT DE NEMOURS AND CO.) 25 April 1935 see page 2, line 107 - page 3, line 125 see page 7; example 1 see figure 1 ---</p>	1,5,7,12
A	<p>WO 95 06763 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 9 March 1995 see page 8, line 24 - line 33 see figure 1 -----</p>	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

• Special categories of cited documents :

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 "E" earlier document but published on or after the international filing date
 "L" document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

15 January 1999

Date of mailing of the international search report

26/01/1999

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/03494

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB 425979	A	FR	755296 A	21-11-1933
WO 9506763	A	09-03-1995	AU 4685497 A AU 686648 B AU 7339194 A CA 2169464 A CN 1130409 A DE 69415025 D EP 0716717 A EP 0844317 A JP 8511304 T ZA 9405848 A	26-02-1998 12-02-1998 22-03-1995 09-03-1995 04-09-1996 14-01-1999 19-06-1996 27-05-1998 26-11-1996 04-02-1996